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# The Effects of FeCl3 Intercalation on the Optical Properties of Multilayer Epitaxial Graphene

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# Abstract

In this study we investigate the effects of intercalation of graphene with Iron III Chloride on the optical and electronic properties of the multilayer graphene. While both the optical properties and the electronic properties of graphene have been previously examined, a viable method of preserving the optical properties while enhancing the electrical properties has not yet been developed. Research has been conducted into the effects of other chemical dopants such as HNO3, but the demonstrated results do not yet provide the high transparency and low sheet resistance required in a transparent conducting electrode. The results from our studies suggest that the decrease in the absorption of the optical wavelengths is a result of the p-doping of the graphene that excludes low energy direct optical transitions. Optical absorption is shown to be both a function of thickness and intercalation staging, as are the electrical properties. The results indicate that intercalating graphene with Iron III Chloride may be a viable method to improve the electronic characteristics of graphene without losing the desired optical properties.

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# 1. Introduction

Graphene, a 2D hexagonal lattice of carbon atoms, has unique electrical and optical properties that make it a leading candidate in the search for a better transparent conducting electrode (TCE). TCEs are a major component in the production of many photovoltaic devices and displays as well as touchscreens. Graphene is both flexible and transparent, ideal qualities in a TCE, but the sheet resistances of graphene grown using current methods is too high for use as a TCE. In order to be considered a feasible alternative to current TCE materials such as indium tin oxide (ITO), the carrier density of graphene must be increased. This reduces the sheet resistance without compromising the optical transparency of the graphene. One method of reducing sheet resistance is chemically doping the graphene via intercalation of iron (III) chloride (FeCl3). Intercalation modifies the band structure of the graphene through doping making it more suitable for use as a TCE material.

### 1.1 Graphene Structure and Properties

A single sheet of graphene, made up of a honeycomb lattice of carbon atoms, can be rolled to form carbon nanotubes (CNTs), while many stacked sheets can form graphite (HOPG), but the materials of interest for this study are the individual layers of isolated graphene.[1] The theoretical properties of a graphene layer have been demonstrated to also exist in both epitaxial and exfoliated graphene on a Silicon Carbide (SiC) substrate.[2] Graphene displays several interesting characteristics that are useful in both industrial applications and in the exploration of 2D phenomena. The charge carriers in graphene, whether electrons or holes, have been demonstrated to share the properties of Dirac fermions with an effective rest mass near zero and velocities on the order of $10^6 m/s$, which is the Fermi velocity $v_F$.3 These charge carriers also exhibit ballistic transport properties; the charge carriers pass through the material with very little resistance due

to scattering. [1,4] An observable quantum hall effect and the Dirac fermions in graphene have provided insights into quantum-electrodynamics (QED) and a tabletop experiment for testing the effects of QED.[1] The high carrier density and high conductivity of graphene have also made it an attractive material for use in next-generation electronics.

Currently there exist three main methods for the production of graphene: mechanical exfoliation, chemical vapor deposition (CVD), and epitaxial growth on silicon carbide (SiC).[1,5,6,7] Graphene has been shown to grow on both the 0001 (Si) and $000\bar{1}$ (C) faces of SiC.[2,8] This process is achieved by heating the SiC to about 1300 $^{o}$C in a medium vacuum environment (~$10^{-5}$ millibars).[7,9] While the graphene grown on the Si-face has a more highly-ordered stacking regime, the growth rate is much slower than on the C-face thereby severely limiting the thickness of the graphene. In contrast the C-face graphene has a much higher growth rate, and a large number of layers can be grown.[9] This is known as multilayer-epitaxial graphene (MEG). In this work MEG was produced using the method first reported by the deHeer group.

### 1.2 Band Structure

The band structure of graphene is that of a semimetal with a pinch in the density of states that effectively acts as bandgap. The band structure displays linear dispersion by the equation

$$E = v_F k \tag{1}$$

where $E$ is the electron energy, $v_F$ is the Fermi velocity, and $k$ is the momenturm vector. The band structure is shown in Figure 1. The pinch in states is known as the Dirac Point and prevents charge carriers from bridging the gap in large quantities, increasing the resistivity of the material. Away

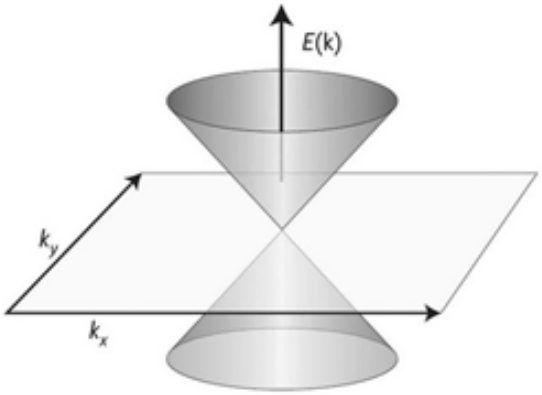



**Figure 1: Band structure of graphene in k-space where the sides of the cones follow the linear equation $E = v_F k$**

from the Dirac Point graphene has increased carrier density and thus decreased sheet resistance. Shifting the Fermi Energy either up or down would move to an area with a higher density of states. This process is known as doping and involves the insertion of charge carriers, whether holes or electrons, into the material. This doping process occurs with no alteration to the band structure or disruption to the bonds between the carbon atoms. A downward shift of the Fermi Energy is known as P-doping the material and corresponds to an increase in the number of positive charge carriers, while an upward shift of the Fermi Energy is known as N-doping the material and corresponds to an increase in the number of negative charge carriers. Doping a material changes the material properties which determine such quantities as carrier density and resistivity. Exposure to air unintentionally dopes most MEG, but this doping is insufficient to lower the sheet resistance to a more desirable level. Chemical doping through intercalation further decreases the sheet resistance by introducing a greater number of charge carriers to the graphene.

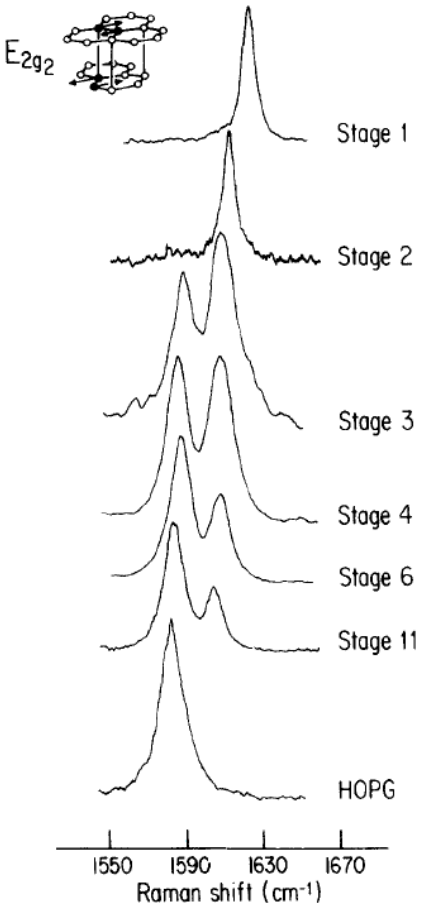
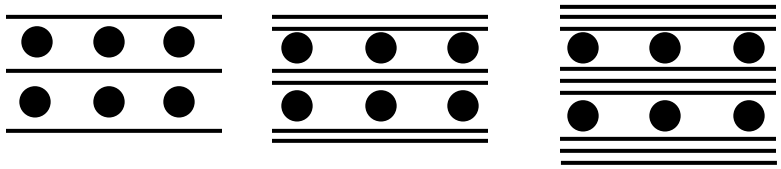



**Figure 3: Raman Spectra for Room Temperature Intercalated Graphite[11]**

### 1.3 Intercalation

Intercalation can be generally defined as the insertion of a different chemical species between the layers of a graphene sample. Intercalation has been previously studied with graphite, but this analysis only provides a general idea of the possible effects of intercalation of graphene and these materials are often not stable in air or are not stable at standard room temperatures.[10] Various stages of intercalation can be achieved with stage one being one layer to intercalant to one layer of graphene while stage two and higher stages

proceed as two layers of graphene to every layer of intercalant and so on (Figure 2). The staging of the sample can be determined through Raman spectroscopy as the G peak is shifted depending on the staging.[11] Raman spectroscopy utilizes the interaction of a laser with any excitations in the system causing a shift in the energy of the laser's photons. Different stages of intercalation have been shown to produce distinctive shifts and splitting in the graphene peak of a Raman spectroscopy plot (Figure 3). [11] Researchers have studied a variety of possible intercalants ranging from noble gases to gold. Nitric acid has been proposed as a possible intercalant for use in TCEs, but it reduces the transparency of the graphene.[12] This work will focus on iron (III) chloride, FeCl3. FeCl3 is stable in air and has a low melting point (315˚C), making it possible to vaporize the FeCl3 without damaging the graphene. The material is also stable at room temperature which allows experiments to be performed without the need for cooling. XPS also shows that the FeCl3 does not chemically bond with the graphene layers.



**(a) Stage 1** **(b) Stage 2** **(c) Stage 3**

**Figure 2: Staging of intercalated graphene. Straight lines are graphene layers and circles are $FeCl_3$ molecules.**

### 1.4 Optical Properties

The phononic properties of MEG, like the electronic properties, have been found to be similar to those of an isolated graphene sheet.[13] The opacity of graphene is defined by the fine structure constant:[14]

$$\alpha = e^2/\hbar c \approx 1/137$$

This constant is associated with the coupling of relativistic electrons and light and is usually seen in quantum electrodynamics. A single graphene layer absorbs 2.3% of incident white light, and when stacked each successive layer also absorbs 2.3%.[14] The optical absorption has been previously reported in detail from the terahertz to the visible range.[13] Of particular concern for TCE materials is the transparency of the visible range, in this case focusing on the range from 300-800 nanometers. The goal of this experiment is to determine the effects of FeCl3 intercalation on the optical properties of 5-10 layer epitaxial graphene.

# 2. Materials and Methods

### 2.1 Graphene Production and Characterization

Multilayer epitaxial graphene was grown on 4H-SiC wafers as previously reported by deHeer.[2,9] The graphene was grown on the carbon face of 3.5-4.5 mm wafers at thicknesses ranging from 13-33Å. The thickness of the graphene sample is dependent on the amount of time spent in the furnace.[2,9] By comparing this time to previously grown and characterized samples, a general idea of the thickness was obtained. In order to determine a precise measurement, however, ellipsometry was used. The ellipsometry measurement was fit using a previously determined trendline in order to determine thickness.[9] Raman spectroscopy was also taken both before and after intercalation.

The electronic properties of the samples were also examined both pre and post intercalation using a four point probe station. Using the methods of Van der Pauw and Hall several values of interest were determined: the resistivity, the mobility, and the Hall resistance.

The Van der Pauw measurements allow us to determine the square resistance, R, of the sample, but they require a correction factor $c$:

$$R = (2.266)(R_1 + R_2)c \tag{2}$$

The Hall Voltage is measured and from this value, $V_H$, the carrier density $n$ can be calculated by:

$$n = I\frac{\frac{0.3}{V_H(1.6\times10^{19})}}{10000}\ cm^{-2} \tag{3}$$

where I and B are known. In order to ensure the data is consistent between measurements, the same phase and lock-in frequency were used.

### 2.2 Intercalation

Intercalation was performed by placing the graphene and anhydrous FeCl3 inside a sealed glass ampoule that was made by closing glass pipettes with a butane torch. Anhydrous FeCl3 was used as hydrated FeCl3 melted at the intercalation temperatures and often came in direct contact with the sample. The sample and the intercalant were separated by bending the ampoule into an L-shape so that only gaseous FeCl3 would make contact with the graphene. In an effort to prevent condensation of FeCl3 on the surface of the graphene the intercalation was first attempted using a two-stage heating system, but independent heating of the sample and the FeCl3 proved to be unnecessary. The ampoule was then heated to between 220˚C and 320˚C,

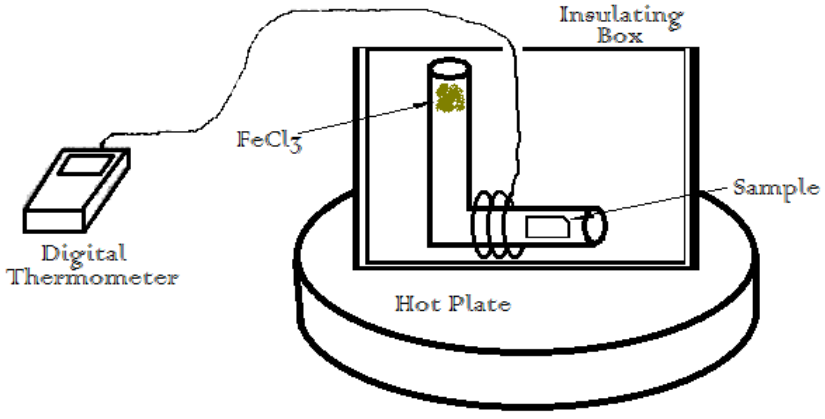



**Figure 3: Intercalation Setup**

allowing the gaseous FeCl3 to intercalate among the layers of the graphene. By adjusting the temperature the intercalation staging could be; this experiment was performed with samples intercalated to stages 1-4. Each sample was allowed to intercalate for 60 minutes before being allowed to cool. Once cooled, the ampoules were broken and the intercalated graphene removed. The staging was confirmed by examining the shift of the Raman G peak.

### 2.3 Photospectroscopy

The optical properties of graphene both before and after intercalation show promise for graphene's potential as a TCE. The optical absorbance of the samples was measured using a Varian Cary 5E UV-vis-NIR Spectrophotometer. Each sample was placed in the spectrophotometer using the thin film holders and air was used as the reference. Two measurements were taken for each sample, both on the carbon face. A range of 800-200 nm was used with a 0.2 second acquisition time with a 1nm spacing measuring absorbance. Two blank SiC wafers were also measured to provide a measurement for background subtraction. The absorption was measured both before and after intercalation.

### 2.4 Heating

In an attempt to clean visible FeCl3 from the surface of the samples they were heated inside evacuated ampoules. The samples were sealed inside ampoules that were evacuated to $\sim 10^{-7}$ torr. These ampoules were then heated to 170˚C for 5 minutes. This temperature was not high enough to deintercalate the samples, but was high enough to remove the visible FeCl3 from the surface of the samples. Once the samples cooled the ampoules were broken and the samples were examined in the Raman to ensure that no deintercalation occurred. The optical measurements were then taken again to determine if the heating had any effect on the absorption properties of the samples.

# 3. Results and Discussion

## 3.1 Pre-Intercalation

The optical properties of the graphene were first confirmed to correspond with previously published results. Using the methods outlined in the previous section the optical absorbance of MEG was measured, and then converted to transmittance (%). This was then plotted as wavelength versus transmittance and as energy versus transmittance. The log of the transmittance was plotted against the number of layers at 500 nm in order to determine the absorbance per layer of the graphene pre-intercalation. The absorbance per layer was then calculated as:

$$\alpha = 1 - 10^{m} \tag{4}$$

Where $m = -0.0108$ is the slope of the best fit line shown in Figure 4.

The graphene was found to absorb ~2.3% of the incident light per layer, exactly as previously reported.[14]

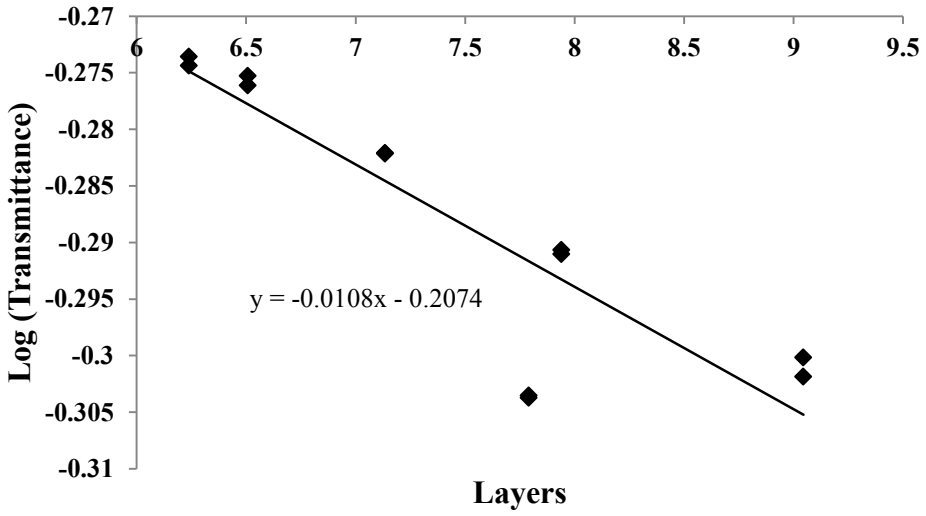



**Figure 4: The log of the absorbance is plotted against the number of graphene layers. The absorbance per layer was calculated as $1 - 10^{-0.0108}$ from the best fit line.**

### 3.2 Post-Intercalation

The absorbance measurements were performed again after the samples were intercalated to a range of stages. The absorbance was plotted as a function of both wavelength and photon energy for each sample. The plot of absorbance vs. photon energy for two samples, one stage 1 FeCl3 intercalated and one stage 3 intercalated, is shown in Figure 5.

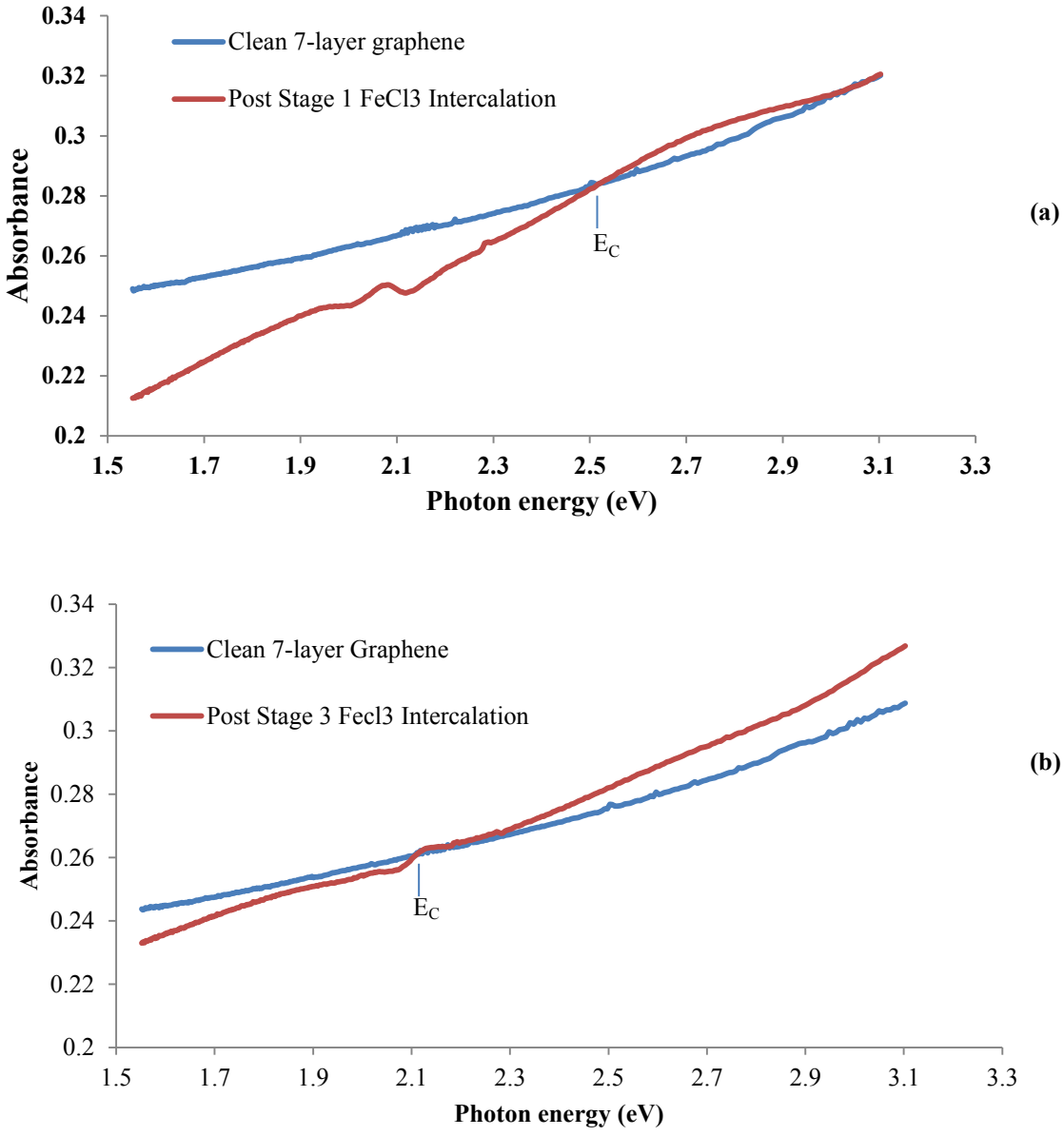



**Figure 5: The plots of two 7-layer graphene samples both before and after FeCl3 intercalation. (a) is a sample that was stage 1 FeCl3 intercalated while (b) was stage 3 intercalated. The photon energy at the crossing point $E_C$ is much higher for the stage 1 intercalated sample.**

The absorbance of intercalated graphene was actually lower than that of the clean samples for photons below a particular energy $E_C$ which is labeled in the plots in Figure 5. When graphene is intercalated with FeCl3 it becomes p-doped. This results in fewer filled states available for electron transition. Without available transitions the graphene is not able to absorb less energetic photons. In order to absorb a photon the electrons must be able to make a vertical transition of energy $2E_D$ as shown in Figure 6. At Stage 1 the sample is more p-doped than at higher stages, so there are less filled states for the electron to transition from so the absorption of the graphene decreases. As the stage increases, the doping of the graphene decreases along with the energy $E_D$. The decrease in $E_D$ allows for more electron transitions which in turn allows for absorption of a greater range of incident photon energies, increasing the absorbance of the graphene.

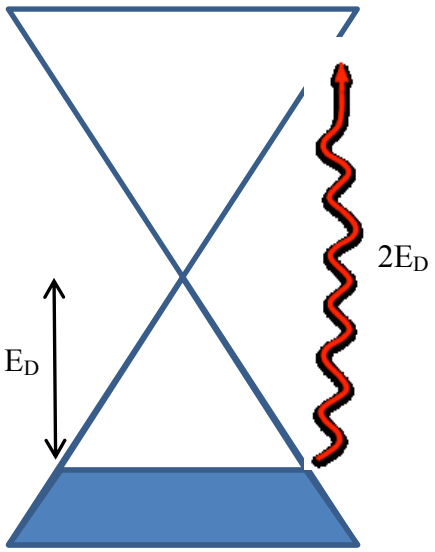



**Figure 6: As the graphene becomes more p-doped there are less filled states available for electron transitions. This results in a lower absorbance of Stage 1 intercalated graphene for photons with energy below $2E_D$. As the stage increases the graphene becomes less doped so the energy $2E_D$ increases and the absorbance of the intercalated sample increases.**

# 4. Conclusion

This work has demonstrated that the intercalation of multilayer epitaxial graphene does not significantly degrade the optical properties that make it a possible candidate for use as a transparent conducting electrode. In fact, the intercalation was shown to decrease the absorbance of the graphene below a photon energy that is dependent on the staging of intercalation. This is most likely due to the p-doping of the graphene excluding low energy optical transitions. While this work lays out preliminary findings about the optical properties, there is not yet enough data to determine more precise values such as absorbance per layer at various stages.

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